

A theoretical study of CO/Cu(100)

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The convergence of the binding energy, geometry, and vibrational frequencies for CO/Cu(100) is studied using a cluster model containing up to 38 Cu atoms. A large basis set is used for the Cu atom at the adsorption site and for the CO molecule. Electron correlation, which is included at the modified coupled-pair functional (MCPF) level, is found to increase the binding energy by about 1 eV. The binding energy and geometry are in very good agreement with experiment for the largest Cu clusters considered. The MCPF binding energies for the smaller clusters can be either larger or smaller than experiment. Unlike the binding energies, the shift in the CO vibrational frequency, relative to free CO, is quite independent of the cluster size or even the inclusion of electron correlation.

I. INTRODUCTION

Recently there have been several theoretical studies of CO on Cu(100). Head-Gordon and Tully¹⁻³ studied the lifetimes of the vibrational modes of CO on Cu(100) and the effect of an electric field on the lifetimes. Bagus and co-workers⁴ have studied the shift in CO frequency with both an applied electric field and with coadsorption of atoms. In both studies¹⁻⁴ a cluster model and the self-consistent-field (SCF) approximation are used to describe the Cu-CO interaction. Both studies yield good agreement with experiment suggesting that they have correctly described the Cu-CO interaction, or at least the change in the interaction with changes in geometry, electric field, and co-adsorption of atoms.

Given the importance of electron correlation in describing⁵ the bonding in Ni(CO)_n and small molecules in general, it is somewhat surprising that studies based on the SCF approximation yield such good results. Nygren and Siegbahn⁶ studied the bonding of CO to small Cu clusters. They found a much smaller oscillation in the CO binding energy with cluster size using a treatment that includes electron correlation than Hermann *et al.*⁷ found using the SCF approximation to model CO/Cu(100). While Nygren and Siegbahn were modeling CO on small Cu clusters rather than CO on Cu(100), they compared their CO binding energy of 0.59 eV for their largest, Cu₂₀, cluster with the experimental result of Tracy.⁸ From Fig. 1 of the paper by Tracy,⁸ it is clear that the binding energy for 0.1 to 0.5 monolayers is 0.58 eV, which is the value that Nygren and Siegbahn compare with. However, at coverages lower than 0.1 monolayers, the binding energy rises to a value of 0.73 eV. We feel that it is more appropriate to compare the cluster calculations to this higher value as they correspond to very low coverage. Thus we conclude that the CO binding energy reported by Nygren and Siegbahn for small Cu clusters is smaller than the value for CO/Cu(100) at low coverage. Part of this difference probably arises from the fact that the absorption site for the Cu clusters does not correspond to the Cu(100) surface. It is interesting to note, however, that their binding energy for Cu₂₀-CO (0.83 eV) is in better agreement with the larger experimental value than is the neutral Cu₂₀ cluster.

Using the local density functional (LDF) approach in conjunction with a slab model, te Velde and Baerends⁹ have studied CO/Cu(100). One advantage of the slab model is that the effect of CO coverage can be studied, whereas cluster models are usually restricted to only the low coverage case. They showed that it was important to have at least a three-layer cluster. While their computed geometry was in good agreement with the somewhat uncertain experimental results,^{10,11} the LDF approach gave binding energies that were too large.

In this work we consider the convergence of the CO binding energy, geometry, and CO vibrational frequency with respect to cluster size using a treatment that includes electron correlation, namely the modified coupled pair functional (MCPF) approach.¹² This approach was shown to be in good agreement with the highly accurate coupled cluster singles and doubles approximation¹³ including a perturbational estimate of the triple excitations¹⁴ [CCSD(T)] and experiment¹⁵ for the triatomic CuCO molecule.¹⁶ The cluster atom positions are taken to be that of the bulk, because we are interesting in modeling CO/Cu(100), not CO on small clusters.

II. METHODS

The C and O basis sets are the correlation-consistent polarized valence triple zeta (cc-pVTZ) sets of Dunning.¹⁷ For Cu we use an all-electron atom at the site of CO interaction and a one-electron effective core potential (ECP) for the surrounding atoms. The ECP parameters and the (4s4p)/[2s1p] valence basis set are those described previously.¹⁸ Note as described below, the *p* functions are deleted from some of the atoms described with the ECP. The all-electron Cu basis set is an atomic natural orbital¹⁹ (ANO) contraction of a large primitive basis set, which is derived from the (20s12p9d) primitive set optimized by Partridge²⁰ for the ²D(3d⁹4s²) state of Cu. This is augmented by three even-tempered *p* functions to describe the 4*p* orbital, an even-tempered 3*d* function to describe the ²S(3d¹⁰4s¹) state, and a (6*f*) set for polarization. This primitive basis is then contracted to [6s5p4d2*f*] based on the average natural orbitals from singles plus doubles configuration-interaction calculations on the ²S and ²D states of Cu. The most diffuse *s* and

p primitives are uncontracted to improve the polarizability. The final contracted basis set is of the form $(20s15p10d6f)/[(6+1)s(5+1)p4d2f]$. Only the pure spherical harmonic components of the basis functions are used in all calculations.

The force constants for the Cu–CO and C–O stretches are computed and the vibrational frequencies determined assuming that the system is a triatomic molecule where the Cu has an infinite mass. Note the C–O frequency is essentially independent of the Cu mass, but the Cu–CO vibration shifts up in frequency if the mass of one Cu atom is used. This is discussed in more detail below.

The calculations were performed using the MOLECULE-SWEDEN program system.²¹ The vibrational frequencies were computed using SPECTRO.²² The calculations were performed on the NASA Ames Central Computer Facility CRAY C90 computer.

III. RESULTS AND DISCUSSION

The metal–CO interaction has been studied in detail for MCO using treatments that included electron correlation.²³ It is known that bonding involves both a σ and π component. The initial σ interaction between the CO 5σ and metal valence electrons is repulsive. Polarization of the metal valence electrons away from the CO reduces this repulsion. The π interaction is attractive with metal to $2\pi^*$ donation leading to significant bonding. This metal to CO $2\pi^*$ donation leads to a positive charge on the metal and hence stabilizes the metal– 5σ interaction. For a single metal atom it is known that the metal to CO $2\pi^*$ donation involves the metal $3d$ electrons and that the inclusion of electron correlation enhances this donation. For one Cu atom it has been found that the Cu $4s$ –CO 5σ repulsion is decreased by Cu $4s4p$ hybridization and bending of the Cu–CO bond.^{16,24} This repulsion leads to a small binding energy of about 0.26 eV.^{15,16} It is clear that the bonding in CO/Cu(100) can be very different from that in the triatomic system; the polarization of the metal valence electrons is expected to be much easier and the metal π donation can come from either the metal $3d$ or the valence electrons. Thus significant differences between CuCO and CO/Cu(100) are expected.

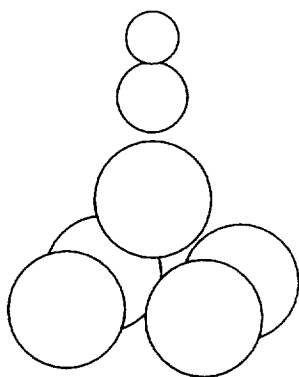


FIG. 1. The $\text{Cu}_5(1,4)\text{CO}$ cluster.

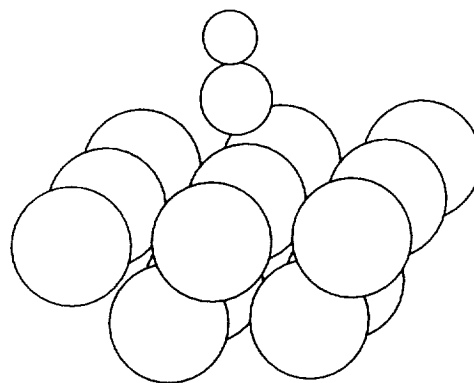


FIG. 2. The $\text{Cu}_{13}(9,4)\text{CO}$ cluster.

The Cu clusters are denoted by the number of Cu atoms in each layer; a 38 atom cluster with 21 atoms in the first layer, 12 in the second, and 8 in the third layer is denoted as $\text{Cu}_{38}(21,12,8)$. The clusters considered are illustrated in Figs. 1–5. The smallest cluster is Cu_5 . This cluster has one Cu atom in the top layer and four in the second—see Fig. 1. The next cluster considered is $\text{Cu}_{13}(9,4)$; relative to $\text{Cu}_5(1,4)$, this cluster adds eight Cu atoms to the first layer—see Fig. 2. Adding one third layer Cu atom, directly below the CO adsorption site, to the Cu_{13} cluster yields the $\text{Cu}_{14}(9,4,1)$ cluster. Adding the four nearest neighbors to the one third layer atom results in the $\text{Cu}_{18}(9,4,5)$ cluster shown in Fig. 3. The $\text{Cu}_{33}(21,12)$ cluster is derived from the $\text{Cu}_{13}(9,4)$ cluster by adding neighbors to the first and second layers—see Fig. 4. These additional atoms are described using the basis set with only s basis functions. Our largest cluster, $\text{Cu}_{38}(21,12,5)$, can be considered as being derived from $\text{Cu}_{33}(21,12)$ by the addition of five third layer Cu atoms—see Fig. 5. This is similar to the five Cu atoms added between $\text{Cu}_{13}(9,4)$ and $\text{Cu}_{18}(9,4,5)$. Alternatively, this $\text{Cu}_{38}(21,12,5)$ cluster, can be considered as being derived from $\text{Cu}_{18}(9,4,5)$ by adding additional atoms to the first and second layers.

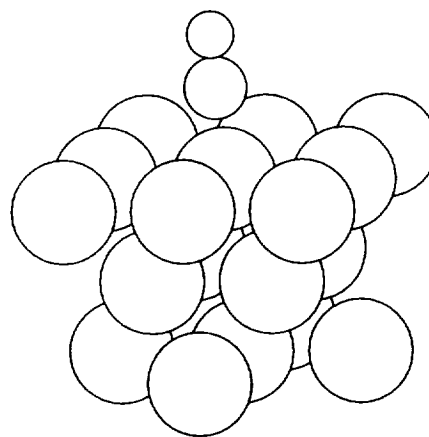


FIG. 3. The $\text{Cu}_{18}(9,4,5)\text{CO}$ cluster. The $\text{Cu}_{14}(9,4,1)\text{CO}$ is formed by including only one atom in the third layer; the central Cu of the five shown in this figure.

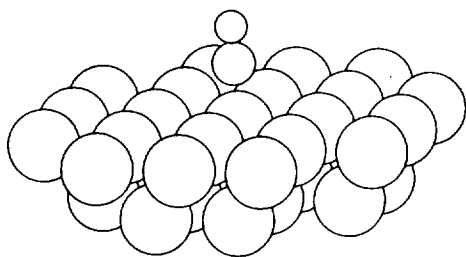


FIG. 4. The $\text{Cu}_{33}(21,12)\text{CO}$ cluster. The nine outermost atoms in the first layer and eight outermost atoms in the second layer are described using only the $4s$ basis set.

We first consider the convergence of the binding energy and geometry with cluster size. While we focus on the MCPF results, we include the $\text{Cu}_5(1,4)$ and $\text{Cu}_{38}(21,12,5)$ SCF results to show the importance of electron correlation in describing these systems. At the SCF level, the Cu_5CO results are in poor agreement with experiment. The Cu–CO bond distance is too long and the Cu–CO binding energy is too small. The Cu–CO distance decreases significantly and the binding energy increases significantly with the inclusion of electron correlation. The D_e value is now clearly too large. This is probably a result of the $4s$ valence electron at the adsorption site being polarized toward the second layer due to the absence of first layer Cu neighbors in this cluster. It is therefore not surprising that adding neighbors in the first layer, to form the $\text{Cu}_{13}(9,4)\text{CO}$ cluster, dramatically reduces the binding energy and increases the Cu–C distance relative to $\text{Cu}_5(1,4)\text{CO}$. Adding one third layer Cu atom increases the binding energy slightly, while adding five third row atoms makes a significant increase in the binding energy—see the $\text{Cu}_{14}(9,4,1)\text{CO}$ and $\text{Cu}_{18}(9,4,5)\text{CO}$ results in Table I. The $\text{Cu}_{18}(9,4,5)\text{CO}$ results are in good agreement with experiment.

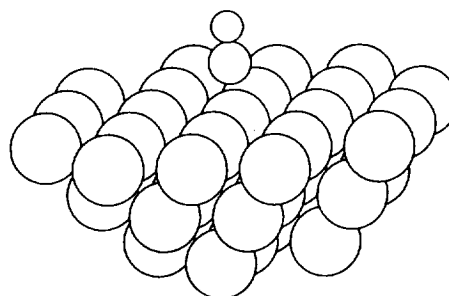


FIG. 5. The $\text{Cu}_{38}(21,12,5)\text{CO}$ cluster. The nine outermost atoms in the first layer and eight outermost atoms in the second layer are described using only the $4s$ basis set.

Removing the third layer, but expanding the size of the first two layers does not significantly affect the binding energy or the geometry. This result might appear to contradict the LDF calculations⁹ that showed three layers are needed to accurately describe the CO/Cu(100) interaction. We suspect that the difference arises from the coverage; we are considering only one CO atom that clearly corresponds to very low coverage where the metal valence electrons in the first and second layers can polarize away from the CO without adversely affecting another CO molecule. This cannot happen for higher CO coverages and therefore polarization into the third layer is very important in reducing the metal–CO repulsion and hence in describing the bonding.

The $\text{Cu}_{38}(21,12,5)\text{CO}$ results show that the polarization into the third layer or in the surface layers is not additive as the results for this cluster are very similar to those for $\text{Cu}_{18}(9,4,5)\text{CO}$ and $\text{Cu}_{33}(21,12)\text{CO}$. This suggests that these clusters are of sufficient size to correctly describe the Cu valence polarization. Because our largest clusters are big enough to describe the polarization and previous

TABLE I. Summary of the MCPF binding energy, geometry, and vibrational frequencies as a function of cluster size. The SCF results for Cu_5CO and Cu_{38}CO are given for comparison. $\Delta\omega_e(\text{CO})$ is the shift in the CO frequency from that in free CO. The bond lengths are in a_0 , the D_e is in eV, and the harmonic frequencies are in cm^{-1} .

Cluster	$r(\text{Cu}-\text{C})$	$r(\text{C}-\text{O})^a$	D_e	$\omega_e(\text{C}-\text{O})^b$	$\omega_e(\text{Cu}-\text{CO})$	$\Delta\omega_e(\text{CO})$
$\text{Cu}_5(1,4)\text{CO}(\text{SCF})$	4.010	2.080	0.39	2361	175	−59
$\text{Cu}_5(1,4)\text{CO}$	3.522	2.154	1.23	2125	350	−60
$\text{Cu}_{13}(9,4)\text{CO}$	3.714	2.145	0.14	2122	245	−63
$\text{Cu}_{14}(9,4,1)\text{CO}$	3.786	2.146	0.23	2114	204	−71
$\text{Cu}_{18}(9,4,5)\text{CO}$	3.632	2.152	0.85	2118	306	−67
$\text{Cu}_{33}(21,12)\text{CO}$	3.581	2.159	0.83	2112	307	−73
$\text{Cu}_{38}(21,12,5)\text{CO}(\text{SCF})$	4.233	2.085	−0.27	2356	105	−64
$\text{Cu}_{38}(21,12,5)\text{CO}$	3.558	2.156	0.78	2120	306	−65
Expt	3.59 ± 0.19^c	2.17 ± 0.19^c	0.73^d	2089^e	339^e	−54
	3.62 ± 0.09^f				345^g	

^aFor comparison, the free CO bond length is $2.087 a_0$ at the SCF level and $2.139 a_0$ at the MCPF level. The experimental (Ref. 28) length is $2.132 a_0$.

^bFor comparison, the free CO ω_e value is 2420 cm^{-1} at the SCF level and 2185 cm^{-1} at the MCPF level. The experimental (Ref. 28) ν is 2143.3 cm^{-1} and ω_e is 2169.8 cm^{-1} .

^cReference 10.

^dThe experiment corresponds to D_0 not D_e , Ref. 8.

^eThe experiment corresponds to the fundamental frequency, Ref. 26.

^fReference 11.

^gThe experiment corresponds to the fundamental frequency, Ref. 25.

TABLE II. Decomposition of the Cu₃₈-CO binding energy, in eV. The CO 2 π^* population is also given.

Constraint	SCF			MCPF		
	D_e	Δ	2 π^*	D_e	Δ	2 π^*
Freeze ^a the central Cu 1s-3d orbitals	-1.06		0.23	-0.40		0.35
Freeze ^b the π orbitals on central Cu	-0.78	0.28	0.24	0.22	0.62	0.38
No constraints	-0.54	0.24	0.27	0.78	0.56	0.50

^aThe Cu 3d electrons are not correlated.^bThe Cu 3d π electrons are not correlated.

calculations¹⁶ on CuCO suggest that this level of theoretical treatment can accurately describe the Cu-CO interaction at the binding site, it is not surprising to find that the computed results for our biggest clusters agree with experiment for binding energy and geometry. Our binding energies are slightly higher than the experiment result. Part of this difference is zero-point energy. If we assume that there is no change in the Cu metal zero-point energy and use the experimental values^{25,26} for the Cu-CO modes, we find a zero-point contribution to the binding energy of -0.05 eV. This brings our Cu₃₈(21,12,5)CO result into fortuitously good agreement with experiment. The Cu-CO geometry is in good agreement with experiment to within their sizeable error bars. The C-O expansion relative to free CO is very small, which is also consistent with experiment.

For Cu₃₈(21,12,5)CO at the SCF level, we find a local minimum above the asymptote. The effect of electron correlation for this cluster is larger than that found for Cu₅(1,4)CO; for example, 1.05 eV vs 0.84 eV in the binding energy and 0.675 a_0 vs 0.488 a_0 for the Cu-CO distance. The increased importance of correlation is probably not surprising because the metal valence charge in the bare Cu₃₈ cluster is not polarized away from the adsorption site. As expected, the Cu₃₈CO results show electron correlation has to be added to obtain reasonable binding energies.

The current calculations yield a much larger electron correlation contribution to the bonding than previous work. For example, the singles and doubles configuration interaction calculations²⁷ correlating only the π electrons in Cu₅(1,4)CO yield a correlation contribution of only 0.27 eV. We attribute the smaller correlation contribution to the lower level of correlation treatment, correlating only some of the valence electrons, and the smaller basis set. For their two largest clusters, Cu₁₀ and Cu₂₀, Nygren and Siegbahn found a correlation contribution to the binding energy of 0.63 eV. This is significantly smaller than found in the present work. This is a little surprising since they correlate the same number of electrons and use a very similar treatment of correlation. We suspect that part of the difference comes from our larger basis set and part from differences in the cluster shapes used in this work and that of Nygren and Siegbahn.

In the limit of infinite clusters, the CO binding energy should be virtually independent of whether the cluster is neutral or has a positive charge. In this regard we note that Nygren and Siegbahn report a binding energy of 0.83 eV for their Cu₂₀CO⁺ cluster. Their Cu₂₀ and Cu₂₀⁺ results therefore bracket the present results. By removing one Cu valence electron, the Cu-CO repulsion is reduced and the binding

energy increased. That is, using the positive ion reduces the repulsion just like increasing the cluster size reduces the repulsion by increasing the polarization. However, the results of Nygren and Siegbahn suggest that using the positive ion does not significantly improve the rate of convergence of the CO binding energy with cluster size.

The C-O ω_e value is significantly reduced by electron correlation, shifting from 2420 cm⁻¹ at the SCF level to 2185 cm⁻¹ at the MCPF level. This latter value is in good agreement with experiment²⁸ (2170 cm⁻¹). This large effect of electron correlation on the C-O ω_e value carries over to the clusters. However, the shift in the C-O frequency in the clusters relative to free CO is hardly affected by electron correlation or by cluster size. The C-O shift varies only from -59 to -73 cm⁻¹ and a few cm⁻¹ of this variation is probably due to errors in the fitting procedure. Thus unlike the binding energy and geometry, this property appears to converge rapidly with cluster size even without the inclusion of electron correlation. It is easy to see why the previous treatments¹⁻⁴ of the CO vibrations have yielded such good result in spite of not including electron correlation.

Unlike the C-O frequency, the Cu-CO frequency is significantly affected by correlation and to a lesser extent by cluster size. The results tend to follow the computed D_e value, as expected. The value for the three largest clusters, 306 or 307 cm⁻¹, is in good agreement with experiment, especially considering that we have used an infinite mass for the Cu cluster. If the Cu mass is reduced the C-O frequency is not changed, but the Cu-CO frequency increases. In the limit that a mass of one Cu atom is used, the Cu-CO frequency is increased to 362 cm⁻¹. Thus we expect that a more rigorous treatment of the vibration would further improve the agreement with experiment for the Cu-CO frequency.

To gain greater insight into the nature of the bonding we decompose the bonding in Cu₃₈CO at the SCF and MCPF levels. The optimal MCPF geometry is used in the decomposition, which is summarized in Table II. In the first step the 1s-3d-like orbitals on the central Cu atom are frozen in their form from the bare Cu₃₈ cluster and only the valence electrons are correlated. In the second step, the π -like orbitals on the central Cu are frozen and the 3d π orbitals are not correlated. The final step is the unconstrained calculation. We first consider the SCF results. When the 1s-3d orbitals are not allowed to relax, the Cu₃₈-CO interaction is repulsive by 1.06 eV. Allowing the Cu σ and δ orbitals or the π orbitals to relax reduces the repulsion by about equal amounts, but the CO is still unbound at the SCF level. There is a small increase in the CO 2 π^* population when the Cu 3d is allowed

to mix with the CO orbitals. Adding valence correlation to the calculation with the Cu $3d$ orbitals frozen does not lead to a bound system. Correlating either the $3d\sigma$ and $3d\delta$ or $3d\pi$ orbitals significantly increases the CO binding energy. These results show that polarization of the metal $1s-3d$ orbitals in both the σ and π spaces are very important in describing the metal-CO interaction. The calculations also show that correlation dramatically increases the importance of both effects. Associated with the correlation of the $3d\pi$ orbitals is a 0.12 electron increase in the CO $2\pi^*$ population relative to correlating only the valence and Cu $3d\sigma$ and $3d\delta$ electrons. This is consistent with previous calculations²³ that showed an increase in the metal to $2\pi^*$ donation with correlation. The $0.024a_0$ increase in the CO bond length for Cu₃₈CO relative to free CO at the MCPF level, compared with the very small ($0.002a_0$) decrease at the SCF level is consistent with the enhanced $2\pi^*$ donation. Thus the insensitivity of the shift in the C-O frequency to the addition of electron correlation is a bit surprising, because the increase in CO $2\pi^*$ donation would be expected to weaken the CO π bond and hence lead to a larger shift in the C-O frequency. One explanation of the results is that 5σ donation to the metal, or at least polarization and stabilization of the 5σ orbital by the increased charge on the Cu, leads to some CO⁺ character in the wave function which increases the CO frequency by about the same amount that the $2\pi^*$ donation decreases it. (The vibrational frequency of CO⁺ is 26 cm^{-1} larger than that of CO.²⁸) Thus there does appear to be some reason to suspect that the insensitivity of the shifts in the CO frequency to electron correlation arises from some cancellation of errors. Given the large increase in the binding energy with correlation, but the small change in the CO frequency, we suspect that part of the increase in D_e with correlation is due to a better description of the dispersion²⁹ between the CO and the Cu $3d$ electrons and by a better description of the electrostatic interaction due to an improved CO dipole moment.

IV. CONCLUSIONS

The convergence of the CO binding energy and geometry show a strong dependence on cluster size for small clusters. The results for the largest clusters are in good agreement with experiment. It is interesting to note that the good results are obtained for both two-layer and three-layer clusters. Thus at low CO coverages, Cu valence polarization can occur ei-

ther along the surface or into the third layer. At higher coverages, it is clear that polarization along the surface will interfere with neighboring CO molecules, so that at higher coverages a third layer will be required, as was found in a recent LDF study of CO/Cu(100). Unlike the binding energy and geometry, the shift in the C-O vibrational frequency, relative to free CO, is nearly independent of cluster size or the inclusion of electron correlation.

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